AN ANALYTICAL TREATMENT OF THE GEOMETRICAL PROPERTIES OF THE THREE-CIRCLE GONIOMETER

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Summary

The use of the three-circle goniometer for X-ray or neutron crystallography is described briefly. Equations are derived using vectorial methods for the computation of the angle settings of the instrument for three-dimensional data collection. These equations are derived for both procedures used in practice, namely, where the (h k l) vector in reciprocal space is brought into coincidence with the scattering vector or when each zone axis [u v w] is brought into coincidence with the axis of rotation of the diffractometer.

I. INTRODUCTION

The three-circle goniometer is a mechanical device with which a rigid body can be given three rotational degrees of freedom. Three rotations are sufficient in general to give any vector referred to axes in the body any arbitrary orientation in space. Its use for crystallographic work was first developed by Furnas and Harker, who fitted it to the standard General Electric X-ray powder diffractometer in order to collect three-dimensional X-ray diffraction data from single crystals while restricting the incident beam and the counter to the equatorial plane. Since then Willis (1961a, 1962) and others have used it for neutron diffraction work, since of the methods available for 3-dimensional data collection, the physical dimensions of the neutron diffractometer make the equatorial plane method the most attractive.

There are two different procedures by which crystallographic data can be systematically recorded. In the first method each (h k l) vector in the reciprocal lattice is systematically brought into coincidence with the scattering vector; in the second each zone axis [u v w] is brought into coincidence with the axis of rotation of the diffractometer and diffraction data for each reflection in that zone are collected by the standard methods used for two-dimensional data collection.

The method used in practice depends on the type of diffractometer available. If a standard X-ray powder diffractometer is used the specimen table usually cannot be disconnected from the counter movement so the first method must be used; however, in the neutron spectrometers of the type in use on the reactor HIFAR the two movements are independent and, since angle setting is carried out by the reactor staff, it is preferable to examine the crystal zone by zone so that only two angles have to be altered to set up each reflection.

In the present paper the instrument is described and the equations required for the computation of angular settings of the instrument deduced by vectorial methods. A geometrical treatment of the first method for using the three-circle goniometer has recently been given by Willis (1961b).

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II. Description of the Three-circle Goniometer

It will be assumed that the incident beam and the counter lie in the horizontal plane and that the angular position of the counter can be adjusted at will to satisfy the Bragg equation for any $(h \ k \ l)$ plane parallel to the vertical axis. The instrument is shown diagramatically in Figure 1. The three circles of the goniometer are the Ω-circle whose axis is along the vertical axis of the diffractometer, the X-circle which is carried on the Ω-circle and whose axis is in the horizontal plane, and the Φ-circle which is mounted on the X-circle and whose axis is the polar axis of the crystal. The rotations about the axes of these circles are designated ω, χ, ϕ respec-
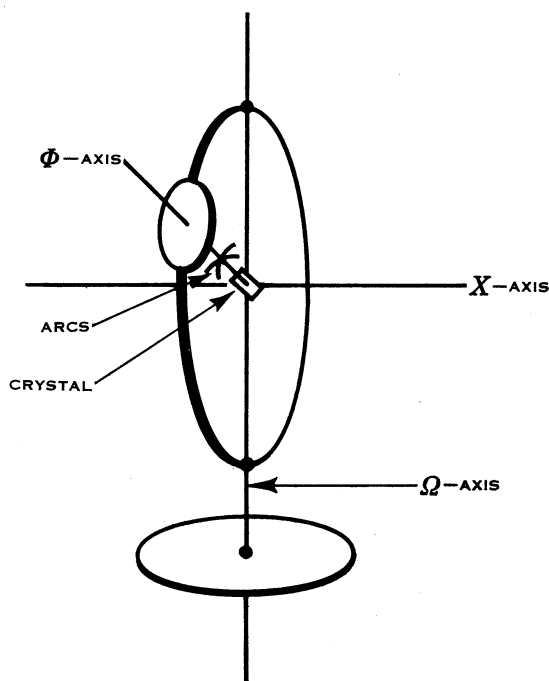

Fig. 1.—Diagram of Φ-, X-, and Ω-circles (after Willis).

tively. Usually the crystal is mounted on goniometer arcs carried on the Φ circle, the motion of these arcs being two additional, unnecessary degrees of freedom.

III. Theory

(a) Geometrical Relationships

Suppose that the vector $\mathbf{r}$ can be brought into coincidence with the vector $\mathbf{r}'$ ($r' = r$) by the single rotation θ. Let the unit vector $\mathbf{m}$ be the axis of rotation and $\mathbf{p}$ and $\mathbf{p}'$ be the projections of $\mathbf{r}$ and $\mathbf{r}'$ onto the plane of rotation. $\mathbf{p}$, $\mathbf{p}'$, and $\mathbf{m}$ form a right-handed system for θ positive.

The projection of $\mathbf{r}$ onto the plane of rotation is the vector perpendicular to $\mathbf{m}$ lying in the $\mathbf{r}\,\mathbf{m}$ plane given by

$$\mathbf{p} = (\mathbf{m} \times \mathbf{r}) \times \mathbf{m}.$$

Similarly,

$$\mathbf{p}' = (\mathbf{m} \times \mathbf{r}') \times \mathbf{m}.$$

$\mathbf{r}$ can be brought to $\mathbf{r}'$ if their projections on the axis of rotation are equal, that is,

$$\mathbf{m}\,.\,\mathbf{r} = \mathbf{m}\,.\,\mathbf{r}' = q \ \text{(say)}. \tag{1}$$

Using (1) and the relations

$$\mathbf{p}\,.\,\mathbf{p}' = pp' \cos\theta,$$

$$\mathbf{p} \times \mathbf{p}'\,.\,\mathbf{m} = mpp' \sin\theta,$$

it follows that

$$\sin\theta = \frac{\mathbf{m}\,.\,\mathbf{r} \times \mathbf{r}'}{r^2 - q^2}, \tag{2}$$

and

$$\cos\theta = \frac{\mathbf{r}\,.\,\mathbf{r}' - q^2}{r^2 - q^2}. \tag{3}$$

(b) Transformation of Direct and Reciprocal Lattice Vectors

To calculate the rotations for a crystal of any symmetry an orthonormal set of axes in the crystal is used. Direct and reciprocal lattice quantities are transformed into this system. A list of the standard relations between the direct and reciprocal lattice is given in the appendix.

The orthonormal axes are defined by:

$$\mathbf{i} = \frac{\mathbf{a}^*}{a^*},$$

$$\mathbf{j} = \frac{\mathbf{c} \times \mathbf{a}^*}{ca^*},$$

$$\mathbf{k} = \frac{\mathbf{c}}{c}.$$

A general vector in the reciprocal lattice is written

$$\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

and a general vector in the direct lattice as

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + l\mathbf{c}.$$

With the aid of the relationships between the direct and the reciprocal lattice these

vectors can be readily written in terms of the orthonormal axes as

$$\mathbf{s} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}, \tag{4}$$

where

$$x = ha^* + kb^* \cos \gamma^* + lc^* \cos \beta^*,$$

$$y = kb^* \sin \gamma^* - lc^* \cos \alpha \sin \beta^*,$$

$$z = l/c,$$

and

$$\mathbf{r} = f\mathbf{i} + g\mathbf{j} + h\mathbf{k}, \tag{5}$$

where

$$f = u/a^*,$$

$$g = vb \sin \alpha - ua \sin \beta \cos \gamma^*,$$

$$h = ua \cos \beta + vb \cos \alpha + wc.$$

IV. CALCULATION OF GONIOMETER ROTATIONS

To make the equations less cumbersome it will be assumed that, at $\omega = \chi = \phi = 0$, which is the initial setting of the instrument, $\mathbf{k}$ is in the vertical direction, $\mathbf{i}$ is along the scattering vector, and the X-axis is at an arbitrary angle ϵ to $\mathbf{i}$. To avoid ambiguity in determining the quadrant in which a particular angle lies all rotations will be expressed in terms of their sine and cosine.

(a) First Method

The vector $\mathbf{s}$ is first rotated about $\mathbf{k}$ to $\mathbf{s}''$ using the Φ-circle and then to $\mathbf{s}'$ by the X-circle. In order that $\mathbf{s}$ can be brought to $\mathbf{s}'$, $\mathbf{s}''$ must satisfy (1) for rotation about the Φ and X-axes.

The X-axis is the unit vector

$$\cos \epsilon \, \mathbf{i} + \sin \epsilon \, \mathbf{j},$$

and therefore

$$(\cos \epsilon \, \mathbf{i} + \sin \epsilon \, \mathbf{j}) \cdot \mathbf{s}'' = (\cos \epsilon \, \mathbf{i} + \sin \epsilon \, \mathbf{j}) \cdot \mathbf{s}'$$

and

$$\mathbf{s}'' \cdot \mathbf{k} = \mathbf{s} \cdot \mathbf{k}.$$

Also,

$$s = s' = s''.$$

Put

$$\mathbf{s}'' = x''\mathbf{i} + y''\mathbf{j} + z''\mathbf{k},$$

then

$$x'' \cos \epsilon + y'' \sin \epsilon = s \cos \epsilon,$$

$$z'' = z,$$

$$x''^2 + y''^2 + z''^2 = s^2.$$

Hence,

$$y''^2 \sec^2 \epsilon - 2sy'' \tan \epsilon + z^2 = 0.$$

Therefore

$$y'' = s \sin \epsilon \cos \epsilon \pm \cos \epsilon \sqrt{(s^2 \sin^2 \epsilon - z^2)}.$$

y'' will be real for $s \sin \epsilon \geqslant z$, so the condition that $\mathbf{s}'$ can be reached from $\mathbf{s}$ is $s \sin \epsilon \geqslant z$.

By substitution,

$$x'' = s \cos^2 \epsilon \mp \sin \epsilon \sqrt{(s^2 \sin^2 \epsilon - z^2)},$$

$$y'' = s \sin \epsilon \cos \epsilon \pm \cos \epsilon \sqrt{(s^2 \sin^2 \epsilon - z^2)},$$

$$z'' = z.$$

The rotations ϕ and χ are then given by (2) and (3) as:

$$\sin \phi = (xy'' - yx'')/(x^2 + y^2), \tag{6}$$

$$\cos \phi = (xx'' + yy'')/(x^2 + y^2), \tag{7}$$

$$\sin \chi = z/s \sin \epsilon, \tag{8}$$

$$\cos \chi = \mp \sqrt{(s^2 \sin^2 \epsilon - z^2)}/s \sin \epsilon. \tag{9}$$

The restrictions on ϵ given by the condition $s \sin \epsilon \geqslant z$ give rise to the three settings discussed by Willis. For $\epsilon = \frac{1}{2}\pi$, the scattering vector lies in the X-plane and all reflections are accessible; for $\epsilon = 0$, the X-axis lies along the scattering vector and only two-dimensional data can be collected. For intermediate values of ϵ a restricted number of reflections can be recorded.

(b) Second Method

To bring the direct lattice vector $\mathbf{r}$ to the vertical position the Φ-circle is used to bring $\mathbf{r}$ to $\mathbf{r}''$, and the X-circle to bring $\mathbf{r}''$ to $r\mathbf{k}$. Applying (1) to both rotations:

$$\mathbf{r}'' \cdot \cos \epsilon \, \mathbf{i} + \sin \epsilon \, \mathbf{j} = r\mathbf{k} \cdot \cos \epsilon \, \mathbf{i} + \sin \epsilon \, \mathbf{j},$$

$$\mathbf{r}'' \cdot \mathbf{k} = \mathbf{r} \cdot \mathbf{k}.$$

Also

$$r = r' = r''.$$

Therefore,

$$f'' \cos \epsilon + g'' \sin \epsilon = 0,$$

$$h'' = h,$$

$$f''^2 + g''^2 = r^2 - h^2,$$

and hence

$$g'' = \cos \epsilon \sqrt{(r^2 - h^2)},$$

$$f'' = -\sin \epsilon \sqrt{(r^2 - h^2)},$$

$$h'' = h.$$

g'', f'', and h'' are real for any ϵ and hence all $\mathbf{r}$ can reach $r\mathbf{k}$.

Again the rotations ϕ and χ are obtained from (2) and (3):

$$\sin \phi = (fg'' - gf'')/(r^2 - h^2), \tag{10}$$

$$\cos \phi = (ff'' + gg'')/(r^2 - h^2), \tag{11}$$

$$\sin \chi = \sqrt{(r^2 - h^2)}/r, \tag{12}$$

$$\cos \chi = h/r. \tag{13}$$

Having placed $\mathbf{r}$ along the vertical axis one can calculate the rotation needed to bring each reflection in the zone $\mathbf{r}$ into coincidence with the scattering vector. The reflection common to both zones is that corresponding to the vector lying along the X-axis after the ϕ rotation. This vector is

$$\mathbf{s}_0 = s \cos(\epsilon - \phi)\mathbf{i} + \sin(\epsilon - \phi)\mathbf{j},$$

and the rotation required to bring it into the position of the scattering vector is

$$\omega = -\epsilon.$$

The setting of the Ω-circle for all reflections $\mathbf{s}$ in the zone $\mathbf{r}$ is then

$$\omega = \omega_0 - \epsilon + \theta_{hkl}, \tag{14}$$

where

$$\sin \omega_0 = \{\sin(\epsilon - \phi)(hx - fz) + \cos(\epsilon - \phi)(gz - hy)\}/sr, \tag{15}$$

$$\cos \omega_0 = \{x \cos(\epsilon - \phi) + y \sin(\epsilon - \phi)\}/sr. \tag{16}$$

V. Conclusion

The settings of the three-circle goniometer for the collection of three-dimensional structure analysis data from a crystal of any symmetry can be found from either equations (4) and (6)–(9) or from equations (5) and (10)–(16), depending on which method is used. Care should be taken to ensure that the same roots of the equations for the components of $\mathbf{s}''$ or $\mathbf{r}''$ are used in the computation of ϕ and χ.

VI. References

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APPENDIX

List of Relationships between the Direct and Reciprocal Lattice

Notation

   a, b, c, lengths of axes of direct cell,

   α, β, γ, interaxial angles in direct cell,

a^*, b^*, c^*, lengths of axes of reciprocal cell,

α^*, β^*, γ^*, interaxial angles in reciprocal cell,

   V, volume of direct cell,

   V^*, volume of reciprocal cell.

Relationships

$$a^* = \frac{bc \sin \alpha}{V}, \quad b^* = \frac{ca \sin \beta}{V}, \quad c^* = \frac{ab \sin \gamma}{V},$$

$$V = abc\sqrt{(1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)},$$

$$VV^* = 1,$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma},$$

$$\cos \beta^* = \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha},$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta},$$

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1,$$

$$\mathbf{a} \cdot \mathbf{b}^* = \mathbf{b} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0.$$